

Claims

- 5 1. A chromium(VI)-free, chromium(III)-containing and
substantially coherent conversion layer on zinc or zinc alloys,
characterised in that
- 10 even in the absence of further components such as silicate,
cerium, aluminum and borate it presents a corrosion
protection of approx. 100 to 1000 h in the salt spray test
according to DIN 50021 SS or ASTM B 117-73 until first
attack according to DIN 50961 Chapter 10;
- 15 it is clear, transparent and essentially colorless and presents
multi-colored iridescence;
- 20 it has a layer thickness of approx. 100 nm to 1000 nm; and
it is hard, adheres well and is resistant to wiping.
- 25 2. A conversion layer according to claim 1, characterised in that
it has across the conversion layer thickness a chromium
content of up to approx. 1%, in relation to zinc and chromium
in the conversion layer an average chromium content of more
than approx. 5%;
- 30 it has a chromium-rich zone > approx. 20% chromium, in
relation to zinc and chromium in the conversion layer, of more
than approx. 15 nm; and
it has a chromium index > approx. 10.
- 35 3. A conversion layer according to claim 1 or 2, characterised in
that it may contain, for further enhanced corrosion protection,

- additional components selected from the group consisting of:
silicate, cerium, aluminum and borate;
- 5 additional metal compounds, in particular 1- to 6-valent metal
compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe,
Ga, In, lanthanides, Zr; Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo,
Hf, Ta, W; and
- 10 anions, in particular halide ions, in particular chloride ions;
sulfurous ions, in particular sulfate ions, nitrate ions;
phosphoric ions, in particular phosphate ions, diphosphate
ions, linear and/or cyclic oligophosphate ions, linear and/or
cyclic polyphosphate ions, hydrogen phosphate ions;
carboxylic acid anions; and silicon-containing anions, in
particular silicate anions; and
- 15 polymers, in particular organic polymers, corrosion inhibitors;
silicic acids, in particular colloidal or disperse silicic acids;
surfactants; diols, triols, polyols; organic acids, in particular
monocarboxylic acids; amines; plastics dispersions; dyes,
20 pigments, in particular carbon black, chromogenic agents, in
particular metallic chromogenic agents; amino acids, in
particular glycine; siccatives, in particular cobalt siccatives;
dispersing agents; and
- 25 mixtures thereof.
4. A conversion layer according to any one of claims 1 to 3,
characterised in that it is a basis for further inorganic and/or
30 organic layers.
5. A conversion layer according to any one of claims 1 to 4,
characterised in that it contains dyes or color pigments for
modification of the inherent color thereof.
- 35 6. A conversion layer according to any one of claims 1 to 5,
characterised in that its layer thickness is approx. 100 nm.

7. A method for producing chromium(VI)-free conversion layers affording at least the corrosion protection of conventional chromium(VI)-containing yellow chromations, wherein
- 5 a metallic surface, in particular one of zinc or zinc alloys, in particular with iron, is treated with a solution of at least one chromium(III) complex and at least one salt;
- 10 **characterised in that**
- the concentration of the chromium(III) complex is increased in comparison with a conventional trivalent blue chromation; and/or
- 15 a chromium(III) complex is used having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.
- 20 8. A method according to claim 7, characterised in that treatment is carried out at an elevated temperature, in particular 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.
- 25 9. A method according to any one of claims 7 or 8, characterised in that the ligands of the chromium(III) complex are selected from the group consisting of:
- 30 chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and
- 35 furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and

- further chelate ligands such as acetylacetone, urea, urea derivatives, and
- 5 further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur (-NR₂, -PR₂, wherein R independently is an organic, in particular aliphatic radical and/or H, and/or -SR, wherein R is an organic, in particular aliphatic radical or H); phosphinates and phosphinate derivatives; as well as
- 10 suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and H₂O and/or
- 15 the method is performed repeatedly on the surface to be passivated.
10. A concentrate for producing a passivation solution for surfaces of zinc or zinc alloys, in particular ones with iron, wherein it substantially contains chromium(III) for a passivating component,
- 20 **characterised in that**
- 25 the chromium(III) is present in the form of at least one complex having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.
- 30 11. A concentrate according to claim 10, characterised in that the chromium(III) complex is selected from complexes with chromium(III) and at least one ligand from the group consisting of:
- 35 chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

- 5 furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and
- 10 further chelate ligands such as acetylacetone, urea, urea derivates, and
- 15 further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur (-NR₂, -PR₂, wherein R independently is an organic, in particular aliphatic radical and/or H, and/or -SR, wherein R is an organic, in particular aliphatic radical or H,); phosphinates and phosphinate derivatives; as well as
- 20 suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and H₂O.
- 25 12. A concentrate according to any one of claims 10 or 11, characterised in that the concentrate is present in solid or liquid form.
- 30 13. A concentrate according to any one of claims 10 to 12, characterised in that it contains further additives selected from the group consisting of: sealers, dewatering fluids; and additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr; Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and
- 35 anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions, phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

- 5 polymers, in particular organic polymers, corrosion inhibitors; silicic acids, in particular colloidal or disperse silicic acids; surfactants; diols, triols, polyols; organic acids, in particular monocarboxylic acids; amines; plastics dispersions; dyes, pigments, in particular carbon black, chromogenic agents, in particular metallic chromogenic agents; amino acids, in particular glycine; siccatives, in particular cobalt siccatives; dispersing agents; as well as
- 10 mixtures thereof.
14. A passivation bath for passivating metal surfaces, in particular ones of zinc, cadmium or aluminum, or alloys of these metals among each other and/or with other metals, in particular with iron,
- 15 **characterised in that**
- 20 it substantially contains chromium(II) as a passivating component, wherein chromium(III) is present in a concentration of approx. 5 to 100 g/l.
- 25 15. A passivation bath according to claim 14, characterised in that chromium(III) is present in a concentration of approx. 5 g/l to 80 g/l, in particular of approx. 5 g/l to 60 g/l, in a particularly preferred manner of approx. 10 g/l to 30 g/l, preferably approx. 20 g/l.
- 30 16. A passivation bath according to claim 14 or 15, characterised in that it has a pH between approx. 1.5 and 3.
- 35 17. A passivation bath according to any one of claims 14 to 16, characterised in that it contains approx. 20 g/l chromium(III) and has a pH of approx. 2 to 2.5.

18. A passivation bath according to any one of claims 14 to 17, characterised in that it contains further additives in particular selected from the group consisting of sealers, dewatering fluids; and
- 5 additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr; Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and
- 10 anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions, and silicon-containing anions, in particular silicate anions; and
- 15 polymers, corrosion inhibitors, silicic acids, in particular colloidal or disperse silicic acids; surfactants; diols, triols, polyols; organic acids, in particular monocarboxylic acids; amines; plastics dispersions; dyes, pigments, in particular carbon black, chromogenic agents, in particular metallic chromogenic agents; amino acids, in particular glycine; siccatives, in particular cobalt siccative; dispersing agents; as well as
- 20 mixtures thereof.
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- 30 19. A passivation bath according to any one of claims 14 to 18, characterised in that it has a bath temperature of approx. 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.
- 35 20. A method for passivating surfaces of zinc or zinc alloys, in particular ones with iron,

characterised in that

the objects to be treated are immersed in a passivation bath according to any one of claims 14 to 19.

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21. A method according to claim 20, characterised in that the immersion period is between approx. 15 and 200 seconds, in particular between approx. 15 and 100 seconds, preferably approx. 30 seconds.

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22. A method according to any one of claims 20 or 21, characterised in that it is an elevated-temperature chromate coating method with rinsing water recycling over at least 2 cascaded rinsing stages.

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23. A method according to claim 22, characterised in that a blue chromation is performed in one of the rinsing steps.

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24. A passive layer obtainable by a method according to at least one of claims 20 to 23.

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25. A passive layer according to claim 24, characterised in that it imparts a corrosion protection to an object such as to present a corrosion protection of at least 100 hours in the salt spray test according to DIN 50021 SS until first attack according to DIN 50961 Chapter 10.,

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26. A passive layer according to claim 24 or 25, characterised in that it presents a greenish, red-green iridescent color for zinc.

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27. A passive layer according to any one of claims 24 to 26, characterised in that its layer thickness is approx. 100 nm.

28. A conversion layer obtainable by a method according to at least one of claims 7 to 9.

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